

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Appl. No. : 10/551,854 Confirmation No. 6166
Applicant (s) : Zenon Lysenko, et al.
Filed : September 30, 2005
5 TC/A.U. : 1621
Examiner : Cutliff, Yate Kai Rene
Title : ALDEHYDE AND ALCOHOL COMPOSITIONS DERIVED
FROM SEED OILS

10 Docket No. : 63104A
Customer No. : 00109

15 Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

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DECLARATION UNDER 37. C.F.R. 1.132

David A. Babb declares and states:

25 THAT, he together with Zenon Lysenko, Donald L. Morrison, Donald L. Bunning,
Christopher W. Derstine, James H. Gilchrist, H. Ray Jouett, Jeffrey S. Kanel, Kurt D.
Olson, Wei-Jun Peng, Joe D. Phillips, Brian R. Roesch, Aaron W. Sanders, Alan K.
Schrock, and Puliikkottil J. Thomas are the inventors of the subject technology of the
above-captioned patent application, and that he is familiar with the Office Action dated
September 26, 2007, in the above-identified application;

30 THAT, in 1982 he received a Bachelors of Science degree in Chemistry from Texas Tech
University, and in 1985 he received a Ph.D. degree in Chemistry from Texas Tech
University;

35 THAT, from 1985 until the current date he has worked at The Dow Chemical Company in
a position of Research Chemist (1985-1993), in a position of Research Leader (1993-
2004), and in the current position of Research Scientist (2004 – present), where he now
leads a project to manufacture and evaluate polyurethanes prepared from polyols derived
from seed oils;

THAT, the following experiments were designed by him and conducted under his supervision for the purpose of comparing an alcohol composition illustrative of the invention having a diol/triol weight ratio greater than 5/1 with a comparative alcohol composition having a diol/triol weight ratio less than 5/1.

5 The above-identified US patent application claims an alcohol composition (hereinafter "monomer alcohol") derived from a precursor aldehyde composition (hereinafter "monomer aldehyde"), which itself is derived from a renewable feedstock comprising one or more seed oils. The claimed monomer alcohol and monomer aldehyde compositions are limited to those comprising a diol/triol and diformyl/triformal weight
10 ratio, respectively, of greater than 5/1. The instant application, at page 18, refers to use of the claimed monomer alcohol composition in the preparation of vegetable oil-based polyols and flexible polyurethane foams, which use is claimed separately in Applicant's International Patent Application Serial no. PCT/US2004/012427, filed April 21, 2004, published as WO 2004/096882 (November 11, 2004), claiming priority from US
15 provisional patent application serial no. 60/465,685, filed April 25, 2003.

Materials for Use in Preparing Polyols

In following Examples 1 and 2 and Comparative Experiment CE-1, the following materials were used.

20 A hydroxymethylated fatty acid methyl ester composition having a diol/triol weight ratio of greater than 5/1 was produced by hydroformylation and reduction of unsaturated soy oil methyl esters, as described in the instant patent application. Further description is given below.

25 A hydroxymethylated fatty acid methyl ester composition having a diol/triol weight ratio less than 5/1 was produced according to the hydroformylation and reduction procedures described in the instant patent application, with the exception that unsaturated linseed oil methyl esters were used in place of unsaturated soy oil methyl esters. Further description is given below.

CEI-625 is a glycerol initiated EO polyol with a number average molecular weight of 625. It was obtained from The Dow Chemical Company.

Irganox 5057 is benzeneamine,-N-phenyl-, reaction product with 2,4,4-trimethylpentene [68411-46-1] obtained from Ciba Co.

Stannous (II) Octanoate [301-10-0] was obtained from City Chemical Co.

5 **Example 1. Preparation of a Polyol Using a Monomer Alcohol of the Invention**

This example illustrates preparation of a polyol derived from a monomer alcohol having a diol/triol weight ratio greater than 5/1 within the scope of the claims. With reference to Applicants' specification, soy oil was hydroxymethylated to form a soy-based monomer alcohol according to the description and examples of the invention. The 10 hydroformylation conditions were similar to those of Example 2 of the application. The resulting monomer aldehyde comprising a mixture of formyl-substituted soy oil methyl esters was hydrogenated under hydrogen in the manner described in the invention, specifically, in the presence of a supported nickel catalyst (Sud-Chemie C-46-8-03) at 120°C and 400 psig (2557 kPa) hydrogen gas to obtain a monomer alcohol composition 15 comprising a mixture of hydroxymethyl-substituted soy oil methyl esters.

The composition of the soy-based monomer alcohol is shown in Table 1, noting that the diol/triol weight ratio was 14.07, according to the claimed range of greater than 5/1.

Table 1. Monomer Alcohol from Soy and Linseed Oils

Component	Ex. 1 and Ex. 2 Soy-Based Monomer Alcohol	CE-1 Linseed-Based Monomer Alcohol
	Weight %	Weight %
Saturates	19.34	49.08
Monols	33.80	20.91
Diols	38.98	13.42
Triols	2.77	4.31
Lactols/Cyclic ethers	1.23	5.20
Lactones	0.62	6.45
Others (including dimers)	3.26	0.63
Total	100.00	100.00
Diol/Triol	14.07/1	3.11/1

The soy-based monomer alcohol composition and initiator CEI-625 were combined in a reactor with stirring, and the oxygen was purged from the reactor by pulling a vacuum on the reactor and refilling the reactor with nitrogen. Catalyst (stannous octanoate) was added to the reactor and agitation was continued. A slow nitrogen sparge was fed to the reactor and the mixture was heated to 195°C while maintaining a vacuum of 80 torr (10.7 kPa). The heating was continued for a minimum of 4 hours under a constant vacuum with a slow nitrogen sweep. The mixture was cooled to 62°C and the antioxidant Irganox 5057 (121 grams) was added with continuing agitation until polymerization was complete. Table 2 sets forth the recipe used to produce the polyol composition and the properties of the polyol resulting therefrom. In the table, the term "M/I ratio" indicates the molar ratio of hydroxymethylated fatty acid methyl ester monomer to initiator. The acronym "Sn(II)" refers to the stannous octanoate catalyst, and "FAME" refers to the fatty acid methyl esters.

Table 2: Polyol Preparation and Properties¹

Ex. #	FAME (kg)	Initiator CEI-625 (kg)	M / I mole ratio	Catalyst (ppm)	Temp (°C)	Run Time (hr)	Viscosity (cP at 25°C)	Hydroxyl percent
1	Soy 26.15	11.8	6:1	Sn(II) (1005)	195/20	12	3940	2.256
2	Soy 26.15	11.8	6:1	Sn(II) (1000)	195/20	12	3570	2.363
CE-1	Linseed 26.20	11.8	6:1	Sn(II) (1005)	195/20	12	1380	1.131

1. FAME[®] refers to fatty acid methyl esters. "M/I ratio" indicates the molar ratio of hydroxymethylated fatty acid methyl ester monomer (M) to initiator (I). "Sn(II)" refers to stannous octanoate catalyst.

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Example 2. Preparation of a Polyol Using a Monomer Alcohol of the Invention

The polyol preparation of Example 1 hereinabove was repeated to form a soy-based monomer alcohol having the composition shown in Table 1. The diol/triol weight ratio of the monomer alcohol was 14.07/1, within the scope of the claims. The monomer alcohol was converted into a polyol in the manner described in Example 1 hereinabove. Polyol results are set forth in Table 2.

Comparative Experiment 1. Preparation of a Polyol Using a Monomer Alcohol

15 Outside the Scope of the Invention

A sample of unsaturated fatty acid methyl esters was hydroxymethylated according to the general hydroformylation/reduction process described Example 1 hereinabove to form a monomer alcohol, with exception that linseed oil was used in place of soy oil and the resulting monomer alcohol had a diol/triol weight ratio less than 5/1.

20 The hydroformylation conditions included reaction of the unsaturated linseed oil methyl esters in N-methyl pyrrolidinone (NMP) (51 weight percent linseed oil methyl ester, 45 weight percent NMP) in the presence of a rhodium-dicyclohexylphenylphosphine monosulfonate sodium salt ligand complex catalyst, at 75-80°C, 300 psi carbon monoxide,

300 psi hydrogen, a [Rh] concentration of 653 ppm, and a ligand/rhodium mole ratio of 15/1 up to a conversion of 85-90 percent. The resulting monomer aldehyde comprising a mixture of formyl-substituted linseed oil methyl esters was hydrogenated under hydrogen in the presence of a supported nickel catalyst (Sud-Chemie C-46-8-03) at 145-150°C and

5 500 psig (3447 kPa) hydrogen to obtain a monomer alcohol composition comprising a mixture of hydroxymethyl-substituted linseed oil methyl esters.

The composition of the linseed-based monomer alcohol is shown in Table 1, where it is noted that the diol/triol weight ratio was only 3.11/1.

The hydroxymethylated linseed oil was thereafter converted into a polyol

10 in the manner analogous to that described in Example 1 hereinabove. Conditions for the preparation are shown in Table 1 hereinabove. A "lard-like" substance (5-10 volume percent) dropped out of the product solution and was discarded. The remaining liquid product was analyzed with the resulting polyol composition set forth in Table 2.

15 **General Procedure for the Production of Polyurethanes from Vegetable Oil-Based (VOB) Polyols**

All polyurethane foam samples were prepared in a consistent manner according to the following general procedure. Chemical components used for the preparation of flexible polyurethane foams included the following materials.

20 Voranol 3137A, which is a 2.7 average functional, 13 wt. percent ethylene oxide, heterofed 3100 MW polyol, was obtained from The Dow Chemical Company.

Water used for these formulations was distilled, deionized water.

D-8264, is an optimized amine catalyst blend for slabstock foam obtained from Air Products & Chemicals, Inc.

25 DC-5160, a flexible slabstock foam silicone surfactant which was obtained from Air Products & Chemicals, Inc.

DABCO T-9, a stabilized stannous octanoate, is a catalyst used in flexible slabstock foams and obtained from Air Products and Chemicals, Inc.

Voranate T-80 is type I TDI (toluene diisocyanate) with an equivalent weight of 87. Used in making flexible foams, it was obtained from The Dow Chemical Company.

5 All of the polyol components of a given formulation were individually metered and weighed into a one quart capacity metal cup. The contents were premixed for 15 seconds at 1800 rpm using a pin type mixer. The tin catalyst, dispensed by volume, was then added to the stirred components and mixed for an additional 15 seconds at 1800 rpm. The cup contents were then poured into a 15 inch x 15 inch x 10 inch (38.1 cm x 10 1. cm x 25.4 cm) wooden box lined with a polyethylene bag. The blowoff time and any other distinct reaction characteristics were recorded. The foam buns were allowed to cure overnight under a ventilated fume hood. They were then placed in ambient storage and submitted for physical property assessment using ASTM test method designation D 3574-95.

15 According to the general procedure, foams were prepared using the following formulations with the results of mechanical testing included in Table 3.

Examples 3, 4, and 5 used vegetable-based polyols obtained from blending the polyols of Examples 1 and 2, which were derived from embodiments of soy monomer alcohol having diol/triol weight ratios of 14.07/1.

20 In Comparative Experiments CE-2, CE-3, CE-4, and CE-5, the vegetable-based polyol was obtained from Comparative Experiment CE-1, which was based on linseed monomer alcohol having a diol/triol weight ratio of 3.11/1.

25 (Refer to Table 3 on next page.)

Table 3 – Preparation and Physical Properties of Polyurethane Foams

Example #	3	CE-2	CE-3	4	CE-4	5	CE-5
Monomer Alcohol Diol/Triol Wt. Ratio	14.07	3.11	3.11	14.07	3.11	14.07	3.11
V-3137	80	80	80	65	65	50	50
Soy Polyol (Blend Ex. 1 & 2)	20	-	-	35	-	50	-
Linseed Polyol	-	20	20	-	35	-	50
Water	4.5	4.5	4.5	4.5	4.5	4.5	4.5
D-8264	0.12	0.14	0.16	0.12	0.16	0.12	0.12
DC5160	1.00	1.00	1.00	1.00	1.00	1.00	1.00
DABCO T-9	0.16	0.14	0.14	0.14	0.16	0.12	0.16
Index ^C	110	110	110	110	110	110	110
Voranate T-80 TDI	57.4	56.5	56.5	58.4	56.1	58.8	55.7
Properties							
Air Flow	4.5	3.6	3.2	4.1	3.0	4.1	4.4
Compression Set 75%	3.5	Tin Split ^A	4.7	Tin Split ^A	7.8	Tin Split ^A	22.5
Density (kg/m ³)	22.8						
40 percent IFD	166.6		23.4		186.4		
Guide Factor	7.3		167.5		8.3		
SAG	2.7		7.2		2.9		
Resiliency (percent)	42	39	36	39	37	39	34
Tensile (kPa)	60	74	92	61	59	75	51
Tear (N/m)	279	188	143 ^B	266	143 ^B	194	205
Elongation	88	112	124	93	72	71	58

A. Comparative foams had tin splits and/or sigh back, which prevented some foam physical properties from being measured.

5 B. Non ASTM, poor samples due to tins splits.

C. "Index" refers to the stoichiometric excess of isocyanate to all hydroxy-containing components of the formulation, i.e., $[NCO]/[OH] \times 100$. An index of 110 means that 10 molar excess of isocyanate is present over all OH equivalents.

10 From Table 3 it is seen that polyols prepared from a monomer alcohol having a diol/triol weight ratio less than 5/1, outside the scope of the claims, produced polyurethane foams with tin splits. Some of the properties of the foams were not measurable and the foams

were unacceptable for use in flexible foam applications, such as furniture cushioning. In contrast, the foams prepared from a monomer alcohol within the scope of the claims having a diol/triol weight ratio greater than 5/1 produced foams without tin splits and having measurable properties within a range acceptable for use in flexible foam

5 applications.

The undersigned DECLARANT declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements are made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application of any patent issuing thereon.

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15 November 20, 2007 Date

David A. Babb